

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 074-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE December 17, 1998	3. REPORT TYPE AND DATES COVERED Annual Technical Report for FY 1998	
4. TITLE AND SUBTITLE Elimination of Toxic Materials and Solvents from Solid Propellant Components (PP1058)			5. FUNDING NUMBERS N/A	
6. AUTHOR(S) Dr. Robert Stanley, Program Manager Ms. Diane Hagler, Program Coordinator				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Aviation and Missile Command Redstone Arsenal, AL			8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP 901 North Stuart St. Suite 303 Arlington, VA 22203			10. SPONSORING / MONITORING AGENCY REPORT NUMBER N/A	
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13. ABSTRACT (Maximum 200 Words) Solid rocket motor (srn) propellant used in military tactical and strategic missile weapon systems contain hazardous and toxic materials. Lead is used as a ballistic catalyst in minimum signature propellants. It's use results in approximately 161,000 pounds of lead compound usage per year. In some "smoky" propellant formulations, hydrogen chloride (HCl) is a combustion product which contributes to stratospheric ozone depletion. It is estimated that seven million pounds of HCL is emitted from military rocket motors per year. Lastly, processing of energetic oxidizer materials used in SRMs requires the use of solvents which are toxic, considered ozone depleting substances and also release volatile organic compounds (VOCs). Approximately four million pounds of oxidizer solvents are utilized in propellant production per year. Due to the human health hazards associated with these toxic compounds, several regulations have been and are being promulgated to curtail or eliminate the use of these substances and their associated emissions. Therefore, alternatives are required to permit future propellant production and maintain weapon system readiness.				
14. SUBJECT TERMS SRM rocket propellant solid rocket motor SERDP PP1058 SERDP Collection				15. NUMBER OF PAGES 10
				16. PRICE CODE N/A
17. SECURITY CLASSIFICATION OF REPORT unclass.		18. SECURITY CLASSIFICATION OF THIS PAGE unclass.	19. SECURITY CLASSIFICATION OF ABSTRACT unclass.	20. LIMITATION OF ABSTRACT UL



SERDP

Strategic Environmental Research
and Development Program

Improving Mission Readiness Through
Environmental Research



Elimination of Toxic Materials and Solvents from Solid Propellant Components (PP1058)

SERDP Annual Technical Report for FY 1998

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Naval Surface Warfare Center, Indian Head

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Department of Energy, Los Alamos

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December 17, 1998

Problem Statement

Solid rocket motor (SRM) propellant used in military tactical and strategic missile weapon systems contain hazardous and toxic materials. Lead is used as a ballistic catalyst in minimum signature propellants. Its use results in approximately 161,000 pounds of lead compound usage per year. In some "smoky" propellant formulations, hydrogen chloride (HCl) is a combustion product which contributes to stratospheric ozone depletion. It is estimated that seven million pounds of HCl is emitted from military rocket motors per year. Lastly, processing of energetic oxidizer materials used in SRMs requires the use of solvents which are toxic, considered ozone depleting substances and also release volatile organic compounds (VOCs). Approximately four million pounds of oxidizer solvents are utilized in propellant production per year.

Due to the human health hazards associated with these toxic compounds, several regulations have been and are being promulgated to curtail or eliminate the use of these substances and their associated emissions. Therefore, alternatives are required to permit future propellant production and maintain weapon system readiness.

Objective

The overall goal of the "Green Missile" program is the elimination of major sources of toxic/hazardous materials used in solid rocket propulsion systems. The objectives are three-fold: 1) develop lead-free extrudable and castable propellant for minimum smoke systems; 2) develop complete and clean burning, HCl-free, combustion of smoky propellant; and 3) develop solventless methods for processing energetic oxidizers.

Technical Approach

Extrudable and castable formulations of ammonium dinitramide (ADN), hexanitrohexaazaisowurtzitane (CL-20), and ammonium nitrate (AN) rocket motor propellants are being developed. The associated energetic polymeric binders, including thermoplastic elastomers (TPE) developed by the CAME program, will also be evaluated and selected for development with the candidate formulations. Data from the characterization of the final formulations shall be compared to baseline data to determine the amount of pollution prevention obtained using the new formulation and that the user requirements for system readiness are still being met. Technology demonstrations are being done for the Tri-Service 2.75 and Army's HELLFIRE systems.

Propellant formulations containing ultra-fine aluminum (UFAL) and non-halogenated oxidizers are being developed and characterized. Formulation studies are being conducted to determine the optimum processing procedures. The combustion efficiency shall be determined as well as the identity of the combustion products to demonstrate clean burning.

A method to produce comminuted ADN, CL-20, and AN oxidizers in a size, shape, and purity suitable for propellant manufacture was developed. Process parameters that influence the behavior of these solvated oxidizers, when crystallized in a liquefied gas anti-solvent, were evaluated and are being optimized. Included in these evaluations were the effects of atomization droplet size, nozzle configuration, oxidizer concentration, solution viscosity, and liquid surface tension on particle size and structure. Process scale-up will be demonstrated with materials to be used for the 2.75 and HELLFIRE systems. Supercritical fluid processing of energetic components will be achieved through supercritical chemistry, supercritical processing and energetic material processing. Technology demonstrations will be done with ADN/CL-20.

Project Accomplishments

Eliminate Lead

Alternatives for lead as a ballistic catalytic have been identified for both castable and extrudable formulations. Approaches evaluated include castable processing using bismuth compounds, lead-free minimum smoke propellant compositions containing oxidizers such as ADN, filled double-base minimum smoke formulations which are extruded and the extruded composite minimum smoke approach.

Both bismuth salicylate and bismuth citrate were evaluated in castable propellant formulations and found to have properties (e.g. Isp, ID) similar to current fielded systems HELLFIRE and JAVELIN. Bismuth salicylate propellants have burning rate properties equal to JAVELIN and superior to HELLFIRE. Propellant specific impulse values are greater than 245 seconds, but less than 250 seconds. Propellant impulse densities are between 15.1 and 15.3. Preliminary signature properties of the bismuth propellants are excellent. Propellant samples containing up to 2% bismuth passed minimum smoke testing with an average of 94%T at 75 degrees and 80% relative humidity. A major discovery in processing bismuth propellants has resulted in extended potlife of fifteen hours or greater. To date, ten pound batches of bismuth propellants have been processed without any potlife problems. Aging tests of both bismuth salicylate and bismuth citrate propellants show n-methyl-p-nitroaniline (MNA) depletion rates comparable to current minimum signature propellants containing lead.

Additional samples of bismuth salicylate and bismuth citrate were purchased from MPC Chemicals (same source used for Pepto-Bismol) and are being evaluated as before. These are cleaner samples (purity >99.99%). Preliminary ballistic property results with the new ingredients are improved. The burning rate pressure exponent appears to be between 0.45 - 0.50 when bismuth citrate is used and is 0.30 with bismuth salicylate. An additional significant advantage of the bismuth propellants is the elimination of the need for heated ovens at 140 degrees F for curing the propellants. Propellants containing either

bismuth citrate or bismuth salicylate will cure at ambient temperatures of 75 degrees F.

Several lead-free minimum smoke propellant compositions have been investigated containing oxidizers such as ADN, CL-20, and triaminoguanidinium nitrate (TAGN) and nitrate ester plasticizers such as 1,2,4-butanetriol trinitrate (BTTN). These propellants contain no combustion additives and no lead. Thermochemical calculations show adequate to excellent performance, and initial measurements on many compositions show promising safety, mechanical, combustion and processing properties. Propellants containing ADN and BTTN-plasticized binders showed a vacuum thermal stability gassing rate at 80 deg. C of 0.12 cc/g/48 hours; this is a relatively low gassing rate for typical BTTN-containing propellants.

Mixed oxidizers are being evaluated in several binders, including: hydroxy-terminated polybutadiene (HTPB) plasticized with butylnitrateethylnitramine (buNENA), 1,2,4-butanetriol trinitrate (BTTN) and trimethylolethane trinitrate (TMETN), glycidyl azide polymer (GAP) plasticized with GAP azide, and poly(diethyleneglycol-4,8-dinitraundecanoate) (ORP-2) plasticized with BTTN and TMETN. Initial safety tests on these propellants showed low impact, friction and electrostatic sensitivities. Thermal properties showed no evidence of thermochemical incompatibility. Initial burn rate measurements in a window bomb showed good burn rates over a range of pressures. The mixed CL-20/ADN formulations showed a somewhat higher pressure sensitivity than propellants containing ADN as the only oxidizer. Optimization of processing, mechanical, and combustion properties is underway.

Lead-free ADN propellants were formulated with ADN produced by Bofors with the collaboration of the scientists at National Defense Research Establishment of Sweden on a low cost synthesis route. This ADN appears to be either plates or needle-like crystals and showed excellent chemical purity. When examined with ion chromatography, the results showed it is at least 99% pure with 0.13% nitrate and 0.03% sulfate as impurities with no nitrite detected. The trace amount of sulfate ion is probably derived from the synthesis reaction.

ADN prills were obtained from the Chemical Systems Division of United Technologies (CSD) under the Integrated High Payoff Rocket Propulsion Technology program. The spherical/ prilled ADN has an average particle size of 300 micron, they are produced from prilling process developed at CSD, which involves molten ADN and mineral oil emulsion technology.

Curing problems during the initial stage of processing these propellants were overcome by using small amounts of nitrocellulose (0.8 - 1.0%) to increase the cross-link density of the propellants. This has resulted in a consistent cure of all propellants made with either neat or prilled ADN materials.

Two series of minimum signature propellant, each using different propellant binders, were made and evaluated with ADN or ADN/CL-20 mixtures. The binders are ORP-2A/BTTN/TMETN and PCP/BTTN/TMETN. A total of four propellants, which consisted of PCP/BTTN/TMETN/ADN(60%), PCP/BTTN/TMETN/ADN/CL-20 (60%), ORP-2A/BTTN/TMETN/ADN (60%) and

ORP-2A/BTTN/TMETN/ADN/CL-20(60%), are currently under study. These materials processed very well, cured properly and void-free samples were achieved. All of these samples were submitted for burn rate characterization. Some of the samples will also be characterized for thermal properties. These results will provide good guidance to optimize further in formulating ADN propellants.

Under the filled double-base minimum smoke approach, two additional propellants were mixed, cast, cured, and extruded. The burn rates for these two approach the desired burn rate for the 2.75" rocket motor. A series of mixes will be processed at 0.2% increments to determine if further increases in high temperature burn rates occur. The mechanical properties for these propellants are acceptable.

A series of six additional cyclotrimethylenetrinitramine (RDX)- filled PNC/BTTN propellant formulations were processed and cast into both lined teflon press tubes and into pan samples for mechanical property determination. After cure, propellant was separated from press tubes, extruded into 1/4" strands on the pilot plant 2" press, cut to length, inhibited, and is currently being tested at -50°F and 150°F. Press tubes have been successfully employed to improve the quality of extruded strands.

Current formulation efforts are geared to determining optimum catalyst level in an unfilled PNC/BTTN propellant in order to match the high temperature burn rate of the reference AA-2 propellant used in the 2.75" rocket motor. The processing matrix employed investigates the effect of increased levels of burn rate catalysts on formulations with either no or low percentages of nitramine (RDX) filler. The goal is to increase the high temperature burn rate of the formulations to more closely match that of the baseline propellant. Two non-leaded catalyst systems are being studied - one employs copper Beta-resorcyate and the other utilizes a ternary system of bismuth subsalicylate, copper salicylate, and carbon black. Previous work on the Green Missile Program has demonstrated that low levels of nitramine incorporation appear to have a beneficial effect on burn rate exponent. Then low levels of nitramine (RDX) will be substituted at the expense of PNC, BTTN and triacetin to determine the effect on ballistic performance.

Under the extruded composite minimum smoke approach, a series of seven additional 1-pint mixes were produced for processing and strand burning rate studies. All the mixes employ an acrylic acid ester (HYTEMP) binder plasticized with dioctyl adipate (DOA) or butyl-NENA. Ratios of ammonium nitrate and CL-20 were traded off against each other to determine how effective CL-20 was as an augmentor of propellant burn rate. The mixes made to date have processed and cured well. Burning rates of the initial mixes are being determined.

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plasticized with DOA or butyl-NENA. Ratios of ammonium nitrate and CL-20 were traded off against each other to determine how effective CL-20 was as an augmentor of propellant burn rate. These mixes are currently being manufactured and will then be characterized.

ELIMINATE HCL

The MLRS booster stage was selected the baseline propellant. The candidate alternative formulation was determined. Four varieties of Ultrafine Aluminum (UFAL) are being characterized. Preliminary tests showed improved combustion using UFAL and ADN than with aluminum and ADN. Propellants containing more than 10% UFAL were difficult to readily process, but propellants made with a blend of UFAL and conventional aluminum were readily processable, even with a total aluminum content as high as 20%.

Several propellant compositions have been made containing ADN and UFAL to evaluate processability, mechanical and combustion properties. Thermochemical calculations on propellant compositions containing ADN and energetic oxidizers predict values of specific impulse that are greater than conventional propellants. Replacing PAO binders with polyazidonitratooxetane copolymer (BAMO/NMMO) raised the specific impulse to 272 s, replacing all the PAO with BAMO/NMMO gave a further increase to 274 s. Initial measurements on propellant samples containing the UFAL made from exploded aluminum wire (ALEX) showed good mechanical properties. Window bomb burning rate tests showed high burn rate pressure exponents of 0.6 and above. Recent work has shown that "fumed" submicron aluminum oxide reduces the pressure exponent in other aluminized propellant formulations to values less than 0.5, therefore, this ingredient is being evaluated in PAO/ADN/Al compositions. One batch of the UFAL from Los Alamos National Laboratory (LANL) showed some outgassing during mixing. The China Lake alane process for producing UFAL is being scaled up to a 25 g scale, which is also being tested.

Compositions containing ADN obtained from Bofors Sweden have been compared with compositions containing ADN produced at China Lake and ADN prills produced by the Chemical Systems Division of United Technologies. Several recent batches of ultrafine aluminum have been tested as well.

Replacement of recrystallized ADN with prills decreased the propellant viscosity from 5 - 15 kPoise to 1.3 kPoise at 115°F. These compositions evolved gas and did not cure. This problem was overcome by dry blending acid scavengers (0.5%) such as triphenylbismuth or tricalcium phosphate with the ADN prills. After standing one day these blends were used to make void-free compositions which had excellent processing and curing characteristics.

Compositions containing ADN typically exhibit burning rate pressure exponent well over 0.5, which generally precludes their use in rocket motors. Compositions evaluated recently have shown that this exponent can be reduced in ADN propellants containing a blend of ultrafine aluminum and conventional aluminum by increasing the particle size of the conventional aluminum. Compositions with conventional aluminum from 5 microns to 60 microns were

tested, and pressure exponents as low as 0.55 were obtained with compositions having 59% solids (approximately 270 sec specific impulse). Based on these findings, this family of ADN compositions provides several promising candidates for further development of energetic, HCl-free propellants.

UFAL was prepared in batches as large as 50 g, with good control of particle size, from 100 to 500 nanometer. These are being tested in propellant compositions, but have shown some gassing and failure to cure. Attempts to eliminate organic impurities for the UFAL or to scavenge reactive groups on the surface of the UFAL have not solved the cure problem. Further characterization of the UFAL and comparison with UFAL from Argonide and Los Alamos is necessary. Characterization of several types of UFAL will be performed at the Air Force Research Laboratory at Edwards Air Force Base.

UFAL will be produced by Indian Head that is similar to that produced by Dr. Joe Martin at LANL in order to provide the Green Missile Program and CAD/PAD with material. Additional funding for this project is coming from the Joint Service CAD/PAD Program, the IM Green Energetics Program and Picatinney Arsenal.

Dr. Martin's method for making UFAL is to use RF induction heating to vaporize aluminum, quickly quench the vapor to form nano-scale material and to passivate with oxygen to form an aluminum oxide coating. We have done an extensive study into how industry vaporizes aluminum. The vast majority of industry uses resistance heating instead of RF induction heating. Dr. Martin started with resistance heat but changed to RF induction because the tungsten boat he was using could not hold up to the corrosive nature of the molten aluminum. A commercially available boat made of boron nitride / titanium diboride was found that can withstand the corrosive environment. They are still an expendable but should last for approximately 15 hours of use and are at a cost of \$20 per boat. Using resistance heating meant that the reactor would have to be redesigned. The redesign work has been completed and all of the necessary parts to install a 20-1000g per hour reactor have been ordered. The reactor is scheduled to be built and running by the end of Jan 99.

CLEAN OXIDIZER PROCESSING

Parameter characterization for solventless processing was completed. Droplet residence time in liquid CO₂ was found to influence particle morphology. Oxidizer concentration had minimal effect on particle size. For nozzle configuration, impingement is superior to fan type. Slower feed rates reduced accretion and generated smaller, smoother crystals. Higher temperatures were also found to produce smaller particles. Scale-up to 1 pound quantities was completed.

The parameters used in the scaled-up particle comminution process with ADN oxidizer have been optimized. The goal to consistently produce high quality ADN particles has been achieved. Due to the chemical instability of ADN, co-precipitations of ADN with stabilizers also have been investigated. Analytical results confirmed the presence of hexamine, a known stabilizer for ADN, in these

co-precipitated, comminuted particles. These comminuted ADN particles in the 10-20 micron range were successfully evaluated in several high performance, minimum signature propellant formulations using micro (25 gram) and pint scale (300 gram) propellant mixers. Energetic GAP and non-energetic Formrez, nitrate ester plasticized propellants have been tested. Significant specific impulse and consistent burning rate increases have been demonstrated with these formulations in comparison to current state-of-the-art propellants. The optimized formulation is now scheduled to be evaluated in 2X4 test motors.

Methods to increase the percent of co-precipitated stabilizer with ADN have continued to be investigated. The goal is to incorporate up to 0.5% stabilizer with the ADN. Also approaches to maximize percent yield of comminuted ADN have been initiated. The miscibility of the ternary mixture of ADN, solvent, and liquefied CO₂ were found to affect the recovery yield. Higher percentage yields of comminuted ADN were obtained when the volumetric ratio of oxidizer solution to liquid CO₂ is decreased. Minimum smoke ADN propellant formulations were tested. The pressure exponents of these high performance ADN propellants were observed to be higher than desired. Several ballistic modifiers have been tested in an attempt to decrease the pressure exponent.

Use of CO₂ for coating molding powders was not satisfactory. Use of propane is being analyzed. The initial set of polymers to evaluate for solventless molding powder processing has been selected on basis of DoD need and technical feasibility. An improved apparatus has been assembled for polymer solubility measurements.

The design of a scaled up (100 g) apparatus for producing coated explosive material (CXM) without the use of solvent is complete. Components have been tested, and the apparatus has been assembled. The apparatus will be installed in the approved test bay and be used to demonstrate the process developed and demonstrated last year at a gram scale. An improved apparatus has been used to evaluate polymer solubility in liquefied and supercritical propane. Initial measurements show that low molecular weight (less than 3000) polystyrene and polyethylene readily disperse and coat the interior of the apparatus under appropriate conditions (approximately 3000 psi and 100 - 110 degrees C), with polymer concentrations up to 2 - 5% depending on temperature and pressure. Low molecular weight polyethylene is of interest in pressed explosives where it may replace wax, if a solventless process for coating RDX is feasible.

TPE DEVELOPMENT FOR SOLID ROCKET MOTORS

Thermoplastic elastomers (TPEs) are being evaluated for use in extrudable minimum signature propellant. Preliminary data suggest a 35/65 hard block/soft block will provide the necessary rigidity.

Three polymeric candidates will be tested against the poly-BAMO/AMMO TPE formulations. Inert simulant propellants of each lead-free candidate are being prepared. Blister peel and other recommended tests will determine "goodness" of adhesion between propellants and candidate insulations. An inert

extruded composite formulation was made and will soon be tested. An inert BAMO/AMMO has been reprocessed into ribbon stock on the 4" and 2" presses for adhesion tests.

Two different polymeric inhibitor systems are being evaluated as potential replacements for the baseline cellulosic inhibitor. These TPE-type systems are based on chemical structures which are expected to confer the ability to significantly retard combustion. The candidates are POSS polyurethanes, and POSS norbornenes (POSS = poly (oligosilsesquioxane)). The POSS norbornene system will be the main research focus, unless it fails the characterization and/or adhesion tests. The POSS polyurethane is the back-up candidate. The initial mechanical properties of POSS-norbornene TPE have been determined as well as the melt flow temperature range of POSS-urethane candidate.

Technical Publications Produced Under the Green Missile Program

Conference/Symposium Proceedings/Papers

- "Minimum Signature Propellants Containing No Lead Catalysts" by May Chan and Alan Turner. 1998 JANNAF Propellant Development and Characterization Subcommittee (PDCS) and Safety and Environmental Protection Subcommittee(SEPS) Meeting. April 21-23, 1998
- "ADN Propellant Technology" published in the Proceedings of Swedish DEA, a technical data exchange agreement meeting with the Defense Research Establishment of Sweden. January 20-23, 1998
- "Particle Comminution by Liquefied Gas Antisolvent Processing" by William Melvin, Joseph McDonald, and Jeffery Wright. 1998 JANNAF PDCS and SEPS Meeting. April 21-23, 1998
- "The Green Missile Program" by Diane Hagler and Pam Carpenter. Keynote address at 1997 JANNAF Safety and Environmental Protection Subcommittee and Propellant Development and Characterization Subcommittee Meetings. March 17-20, 1997
- "High Performance Lead-Free Minimum signature Propellant Development" by Larry Warren. 1998 JANNAFPDCS and SEPS Meeting. April 21-23, 1998
- "High Performance Lead-Free Minimum Signature Propellant Development" by Larry Warren. Joint JANNAF Propulsion Meeting. July 1998
- "Evaluation of Bofors' AND" published in the Proceedings of Swedish DEA, a technical data exchange agreement meeting with the Defense Research Establishment of Sweden. November 16, 1998

Published Technical Abstracts SERDP Annual Symposium

- "Green Missile Program" by Diane Hagler. 1998 Strategic Environmental Research and Development Program Technology Symposium and Workshop. December 1-3, 1998.